Journal of Colloid and Interface Science 351 (2010) 102–107

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Silicone oil emulsions stabilized by semi-solid nanostructures entrapped at the interface

Yoon Sung Nam [a,b,*], Jin-Woong Kim [b,**], Jongwon Shim [b], Sang Hoon Han [b], Han Kon Kim [b]

[a] *Department of Biological Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA*
[b] *Amore Pacific R&D Center, 314-1 Bora-dong Giheung-gu Yongin-si, Gyounggi-do 449-729, Republic of Korea*

ARTICLE INFO

Article history:
Received 24 May 2010
Accepted 3 July 2010
Available online 11 July 2010

Keywords:
Block copolymers
Amphiphilic copolymers
Emulsions
Colloidal stability
Poly(ε-caprolactone)

ABSTRACT

Oil-in-water (O/W) emulsions are typically stabilized using water-soluble surfactants, which anchor to the surface of oil droplets dispersed in an aqueous solution. The structure of the anchored surfactants is often susceptible to physical and chemical stresses because of their highly mobile properties. Here we introduce a new approach to prepare stable silicone oil emulsions under various external stresses using a water-insoluble amphiphilic block copolymer, poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL). Above the melting temperature (around 60 °C) of the hydrophobic segment (PCL), PEO-*b*-PCL can be dissolved in silicone oil. When the polymer/oil mixture is dispersed in water, PEO-*b*-PCL is irreversibly reorganized into solid nanostructures at the interface of the aqueous/organic phases. The resulting interfacial structures provide a robust physical barrier to the emulsion coarsening processes. Accordingly, the prepared emulsions exhibit excellent structural tolerance against external stresses, including variations in pH, ionic strength, and temperature.

1. Introduction

Amphiphilic molecules are used to stabilize emulsion droplets by reducing the interfacial energy between two phases. A combination of multiple interactions is often involved in the stabilization process, including electrostatic interactions, steric hindrance, the Marangoni effect, and mechanical forces [1–4]. Small molecular weight surfactants quickly alternate between adsorption and desorption at the interface and readily migrate on the surface of droplets. Because of such dynamic properties, an excess amount of surfactants is usually used to maintain the colloidal stability of emulsions. However, for biological applications, the use of large amount of surfactant can cause adverse responses and even cellular toxicity because cellular membranes are prone to disintegration as they strongly interact with molecular surfactants [5–7]. In addition, surfactants are diluted to a large extent when they are administrated into our body for *in vivo* therapy or dispersed in culture media for *in vitro* biological testing. This dilution decreases the effective concentration of surfactants and thus destabilizes emulsion structures. Therefore, macromolecular emulsifiers (e.g., polymers, proteins, particles, etc.), which show multivalent interactions and a low critical micelle concentration (c.m.c.), have been suggested as alternatives to small molecular weight surfactants [8–14].

Macromolecular emulsifiers have several unique properties, including relatively good biological tolerance, low foaming, good chemical and mechanical stabilities, and stimuli-sensitive reversible responses [14–16]. In addition to biological applications, the interfacial behaviors of amphiphilic macromolecules have been extensively investigated in the petroleum industry because they are relevant to two problems in crude oil production, which are the stability of water-in-oil emulsions and the deposition of crude oil fractions on metal surfaces [17–19]. A number of amphiphilic copolymers have been successfully commercialized as emulsifiers in a broad range of industrial practices [14,20]. In most cases, the steric stabilization has been known as a major mechanism of polymeric emulsifiers. The size and solubility of the corona segments of the polymers, which are exposed to the continuous phase, are critically important for the colloidal stability of emulsions [21,22]. It was also revealed that the emulsion stability is greatly affected by the extent to which polymers diffuse to a dispersed phase and the molecular shape of polymer chains at the interface [21–25]. For instance, PEO-*b*-PPO (polyethylene oxide-*block*-polypropylene oxide) can stabilize cyclohexane/water emulsions through the deep penetration of the PPO block into the organic phase. The PPO block is shielded from unfavorable interactions with water molecules, and this shielding effect reduces the intramolecular association between the PPO and the PEO blocks. Such configura-

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* Corresponding author at: Department of Biological Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.
** Corresponding author.
E-mail addresses: yoonsung@mit.edu (Y.S. Nam), kjwoong@amorepacific.com (J.-W. Kim).

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doi:10.1016/j.jcis.2010.07.005

tion allows a more extended conformation of PEO in the aqueous phase, enabling more effective repulsion between neighboring chains. Therefore, it is now widely accepted that, to successfully stabilize emulsions, the hydrophobic segment of a polymeric emulsifier needs to be highly soluble in the organic phase while the hydrophilic segment provides steric hindrance through the extension toward the aqueous phase [21,25].

Here we introduce an emulsion system based on an amphiphilic block copolymer having a hydrophobic segment that is not soluble in the organic phase, resulting in the solidification of the block copolymer at the interface. This approach is illustrated using an amphiphilic diblock copolymer, poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL). PCL is a semi-crystalline polymer with a relatively low melting temperature (T_m) around 60 °C and is not soluble in commonly used oils under ambient conditions. Both of the polymers are well known to be biodegradable and biocompatible, and thus are widely used for biological applications [26–30]. PEO-*b*-PCL was dissolved in ethanol around 60 °C, and this solution was readily miscible with phenyl trimethicone (PTM). PTM is a clear, odorless silicone oil widely used in personal care and cosmetics products because of its water repellency, good alcohol compatibility and inertness [31,32]. When this polymer/oil mixture was dispersed in pure water, alcohol molecules diffused out to the external aqueous phase while PEO-*b*-PCL formed semi-solid, amphiphilic nanostructures at the interface. It was anticipated that the formation of a solid polymer layer at the oil–water interface would effectively stabilize the emulsion structure against physical and chemical stresses. The morphology and rheological properties of the prepared emulsion were compared to those of the emulsion prepared by a widely-used commercial polymeric emulsifier, poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO_{106}-PPO_{70}-PEO_{106}, Pluronic® F127). Pluronic F127 has an average molecular weight of 12.6 kDa, a T_m of 56 °C, and water solubility higher than 10% at 25 °C. The colloidal stability of the emulsions prepared with PEO-*b*-PCL was also examined in the presence of stresses induced by the variations in pH, ionic strength and temperature.

2. Experimental section

2.1. Synthesis and characterization of PEO-b-PCL

To synthesize a PEO-*b*-PCL diblock copolymer, the ring opening polymerization of ε-caprolactone was carried out using methoxy PEO (5 kDa) (Fluka Chemie GmbH, Buchs, Switzerland) as an initiator. The reaction mixtures were prepared by introducing ε-caprolactone into a silanized flask containing methoxy PEO and stannous (II) octoate ($Sn(Oct)_2$, Sigma–Aldrich). The flask was evacuated, sealed off and placed at 120 °C for 24 h. The resulting polymer was dissolved in methylene chloride and precipitated in an excess of cold methanol. The precipitated polymer mass was dried under vacuum for 3 days. ^1H nuclear magnetic resonance (NMR) spectrum was obtained at 25 °C with a Gemini-300BB NMR operating at 300.06 MHz using $CDCl_3$ as a solvent. Chemical shifts were measured in parts per million using tetramethylsilane as an internal reference. The molecular weight of the synthesized polymer was determined using gel permeation chromatography (GPC). A high performance liquid chromatography (HPLC) system composed of Agilent 110 series (Agilent Technologies, Palo Alto, CA, USA) and refractive index detector was operated at 1.0 mL min^{-1} using a series of three PLgel columns (300 × 7.5 mm, pore size = 103, 104, and 105 Å) as size exclusion columns. Tetrahydrofuran was used as an isocratic mobile phase, and monodisperse polystyrenes were used as calibration standards.

2.2. Emulsification of silicone oil-in-water

One gram of PEO-*b*-PCL was dissolved in absolute ethanol (3 mL) with magnetic stirring at 500 rpm at 70 °C for about 5 min. PTM (Shin-Etsu Chemical Co., Japan, 10 mL) pre-equilibrated to 70 °C was mixed with the polymer solution by magnetic stirring at 500 rpm for about 20 s. The mixture of PEO-*b*-PCL and PTM was emulsified in Milli-Q water (18.2 Ω cm) at 70 °C using a T.K. homo-mixer Mark II f model (Tokushu Kika Co. Ltd., Osaka, Japan) at 5000 rpm.

2.3. Fluorescent labeling of PEO-b-PCL

The terminal hydroxyl group of PEO-*b*-PCL (10 μmoles) was reacted with 50 μmoles of 1,1′-carbonyldiimidazole (CDI, Sigma–Aldrich) in 1 mL anhydrous acetonitrile at room temperature for 1 h. Fluorescein amine (10 μmoles, Sigma–Aldrich) in anhydrous acetonitrile was added to the polymer solution followed by the incubation at room temperature for 12 h. Residual imidazoles were removed by dialysis (Spectra/Por® membrane 4, molecular cutoff: 12–14 kDa, Spectrum) against Milli-Q water at ambient temperature in the dark for 2 days. The fluorescein-labeled PEO-*b*-PCL was then freeze-dried and kept at 4 °C until use.

2.4. Microscopic observation

The droplet morphology of the prepared emulsions was observed with an optical microscope (OM, Olympus BX50, Olympus Optical Co. Ltd., Tokyo, Japan). The emulsions stabilized with fluorescently labeled PEO-*b*-PCL were examined on a confocal laser scanning microscope (CLSM, model LSM 510, Zeiss, Jena, Germany). Surface morphologies of the emulsions were examined on a scanning electron microscope (SEM, Hitachi S-4300) operated at 5 kV. Emulsion samples were placed into a cylindrical tube, rapidly frozen using liquid nitrogen slush, and transferred to a SEM cryogenic chamber system (Hitachi S-4000 series). To analyze the emulsion morphology using transmission electron microscopy (TEM), a drop of the sample was placed onto a 100 mesh copper grid coated with carbon (Ted Pella, Inc.). After deposition, the grid was tapped with a filter paper to remove surface water and negatively stained using a 1% uranyl acetate solution. The samples were dried in air for about 1 h before measurement. TEM analysis was performed on a JEOL 1010 electron microscope (Akishima, Japan) operated at 200 kV.

2.5. Emulsion stability

Physical stability of the prepared emulsions was estimated using a two-point conductivity method with a DualCon stability tester (ITEC-IFAC Technology GmbH & Co. KG, Duisburg, Germany). Two pairs of electrodes determined the conductivity at the top (κ_1) and at the bottom (κ_2) of the sample placed in a cylindrical container. The conductivity difference ($\Delta\kappa = \kappa_2 - \kappa_1$) between these values was used to determine the colloidal stability of the prepared emulsions. The schematic description of the two-point conductivity measurement is shown in Fig. S1.

2.6. Rheological analysis

Stress-controlled rheological analysis was carried out using a Bohlin C-VOR Rheometer (Bohlin Instruments Inc., East Brunswick, NJ, USA) at 25 °C using a concentric cylinder with a gap of 2.5 mm. Stress was applied to the sample by rotating the outer cylinder. The torsion exerted on the inner cylinder was measured by a 0.35 g torsion bar, connected to an electromagnetic transducer.

3. Results and discussion

PEO-*b*-PCL was synthesized by the ring opening polymerization of ε-caprolactone with methoxy PEO. The weight ratio of PCL to PEO was 2.3, as measured using ^{1}H nuclear magnetic resonance spectroscopy (Fig. S2). The weight average molecular weight and the polydispersity were 16.6 kDa and 1.37, respectively. PEO-*b*-PCL (1 g) was dispersed in several different oils (40 mL) with bath sonication for 1 h and placed in an oven for 2 days without agitation at 80 °C. The phase separation was observed even at the elevated temperature, indicating the immiscibility of the polymer with the oils. The aliquot of sample was then carefully taken from the upper phase (an oil-rich phase) for GPC analysis, but no trace of PEO-*b*-PCL was detected under the detection limit (*ca.* 0.05 wt.%). In order to thoroughly disperse PEO-*b*-PCL in the oil, the polymer (1 g) was first dissolved in ethanol (3 mL) around 50 °C. Above 70 °C, the polymer solution was readily miscible with PTM (10 mL) to form a homogeneously transparent solution. The solution became turbid as the solution was cooled to ambient temperature. When the solution was cooled, spherulitic crystalline domains of PEO-*b*-PCL wetted by PTM were observed under polarized optical microscopy (Fig. 1a and b). The micron-sized polymer structures were collected by centrifugation (10,000×*g*, 20 min) in order to examine their thermal properties using differential scanning calorimetry (DSC). The melting temperatures of PEO-*b*-PCL dispersed in PTM were 47.3 °C (the lower T_m) and 52.6 °C (the higher T_m). The values were significantly lower than those of dry PEO-*b*-PCL powder, 52.1 °C and 56.3 °C (Fig. 1c). These results indicated that PEO-*b*-PCL was not dissolved in the organic phase at ambient temperature; however, the crystalline structure of PCL was slightly affected by the wetting of the polymer in the oil.

Although PEO-*b*-PCL can be completely dissolved in a pure silicone oil at an elevated temperature, the solubility of PEO-*b*-PCL can be different within the oil droplets dispersed in an aqueous phase. In emulsions, a trace amount of water molecules can be partitioned to the organic phase and play as a non-solvent that decreases the solubility of PEO-*b*-PCL in the oil, resulting in non-solvent-induced phase separation. However, direct observation of such phase changes in a micron-sized oil droplet is very difficult because of the small droplet size. Therefore, the effect of water on the phase behavior of PEO-*b*-PCL in the organic phase was examined using the macroscopically separated layers of the organic and aqueous phases. To this end, PEO-*b*-PCL was dissolved in a mixture of ethanol and PTM at 70 °C as described above, and then at the same temperature, pre-warmed water was slowly added to the organic solution without any agitation. The organic phase became turbid, indicating the oil-polymer demixing in the organic phase. This solid–liquid phase separation seems likely to occur as the PCL block became frozen as water molecules diffused into the organic phase. Water worked as a non-solvent that decreased the miscibility of PEO-*b*-PCL with the silicone oil. These results indicate that the polymer chains need to migrate toward the interface quickly before water molecules penetrate into the organic phase. Otherwise, PEO-*b*-PCL can be solidified and precipitated within the organic phase. To prepare stable silicone oil-in-water emulsions, 13 mL of the organic phase consisting 1:3:10 mixture of PEO-*b*-PCL:ethanol:PTM were vigorously homogenized at 5000 rpm into 87 mL of Milli-Q water pre-warmed at 70 °C. Fig. S3 indicates that the emulsion size initially decreased with increased duration of homogenization, but did not show further apparent changes after 5 min of homogenization. For the rest of the experiments in this report, the homogenization period was fixed at 15 min.

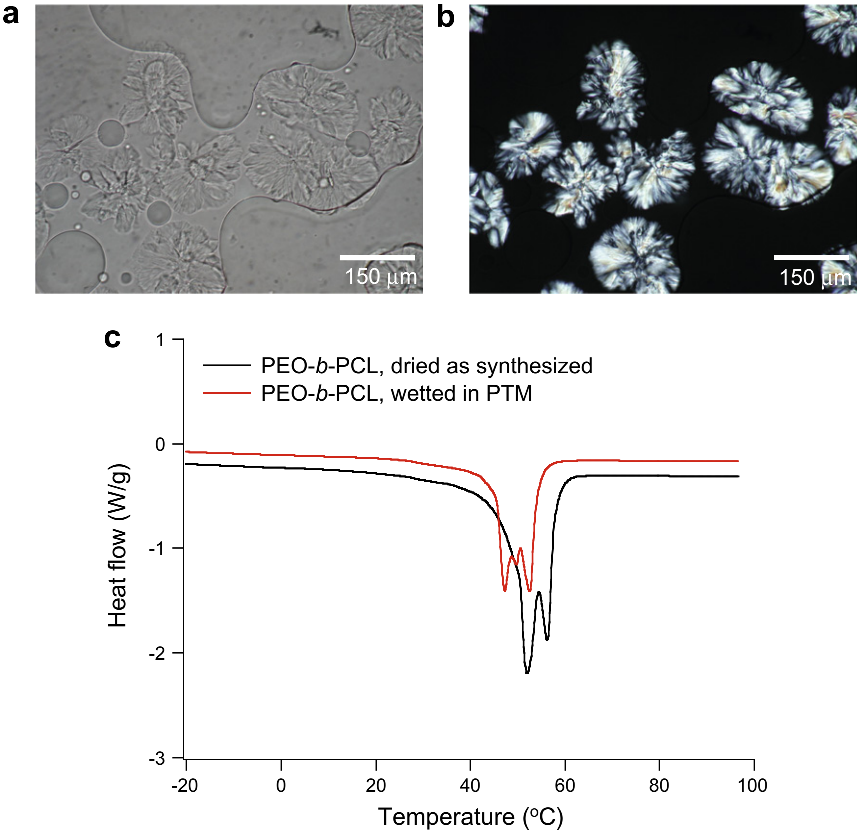

Fig. 1. (a) Bright-field and (b) polarized optical micrograph of PEO-*b*-PCL in PTM at ambient temperature, and (c) differential scanning calorimetry diagram of PEO-*b*-PCL as synthesized (black) and wetted in PTM (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To visualize the distribution of PEO-*b*-PCL in the emulsion, the polymer was fluorescently labeled by conjugating fluorescein amine (Sigma–Aldrich) to the hydroxyl terminal group of PCL via a carbamate linkage using 1,1′-carbonyldiimidazole (CDI) (Fig. 2a). Confocal fluorescence micrograph of the emulsions stabilized by PEO-*b*-PCL shows that PEO-*b*-PCL was predominantly located at the interface between the aqueous and the organic phases as indicated by an arrow in Fig. 2b. This is interesting because the polymer was originally dissolved in the organic phase. In general, the oil-in-water emulsions are stabilized by amphiphilic molecules, which are dissolved in the continuous, aqueous phase and migrate toward the surface of emulsions followed by adsorption. The emulsions were observed under transmission electron microscope (TEM) in order to examine the morphology of PEO-*b*-PCL in the emulsions. Prior to the TEM analysis, large emulsion droplets were removed by centrifugation at 2000×*g* for 5 min and only the supernatant was placed on a carbon-coated copper TEM grid. A mixture of core–shell type nanoparticles and oil-filled nanostructures were observed around the circular, darker regions, which seem to be the trance of the small oil droplets in the supernatant of the emulsion sample (indicated by arrows). The TEM image implies the possibility that PEO-*b*-PCL in the organic phase migrated or co-diffused with the oil toward the aqueous phase, resulting in the entrapment of oil/polymer nanoparticles at the interface. This explanation was also supported by cryogenic scanning electron micrographic (SEM) analysis, which exhibits small protrusions on the surface of the emulsions stabilized by PEO-*b*-PCL (Fig. 3b and c) while the emulsions stabilized by PEO-*b*-PCL showed a smooth surface (Fig. 3a). These structures might be derived from the phase segregation of PEO-*b*-PCL in the organic phase as water molecules diffused into the organic phase, inducing the change in the miscibility of the block copolymer with the silicone oil. As the PEO chains were exposed to the aqueous phase, PEO-*b*-PCL seemed to self-associate to form amphiphilic aggregates stabilizing the oil–water interface.

Fig. 4a shows the rheological responses of the O/W emulsions stabilized by PEO-*b*-PCL nanostructures to small amplitude oscillatory shear flows. Both the elastic and viscous moduli (G' and G'') of the emulsions stabilized by PEO-*b*-PCL were about three orders of magnitude smaller those that of the Pluronic F127-based emulsions. The oil content and the concentration of the emulsifiers were 10 wt.% and 1 wt.%, respectively, for both of the emulsions. In addition, the emulsions stabilized by Pluronic F127 showed a shear-thinning behavior above 0.2 Pa of shear stress, while PEO-*b*-PCL emulsions exhibited the Newtonian behavior over the entire range of shear stress examined. High modulus values and apparent shear-thinning behavior of the emulsions stabilized by Pluronic F127 seem to be caused by the inter-droplet interactions and the following structural breakdown of the network with the applied shear forces [33]. The uniform resistance of the PEO-*b*-PCL emulsions against flow implies the little deformation of the interfacial structures by shear forces, implying that PEO-*b*-PCL aggregates form a mechanically stable film on the surface of emulsions [34].

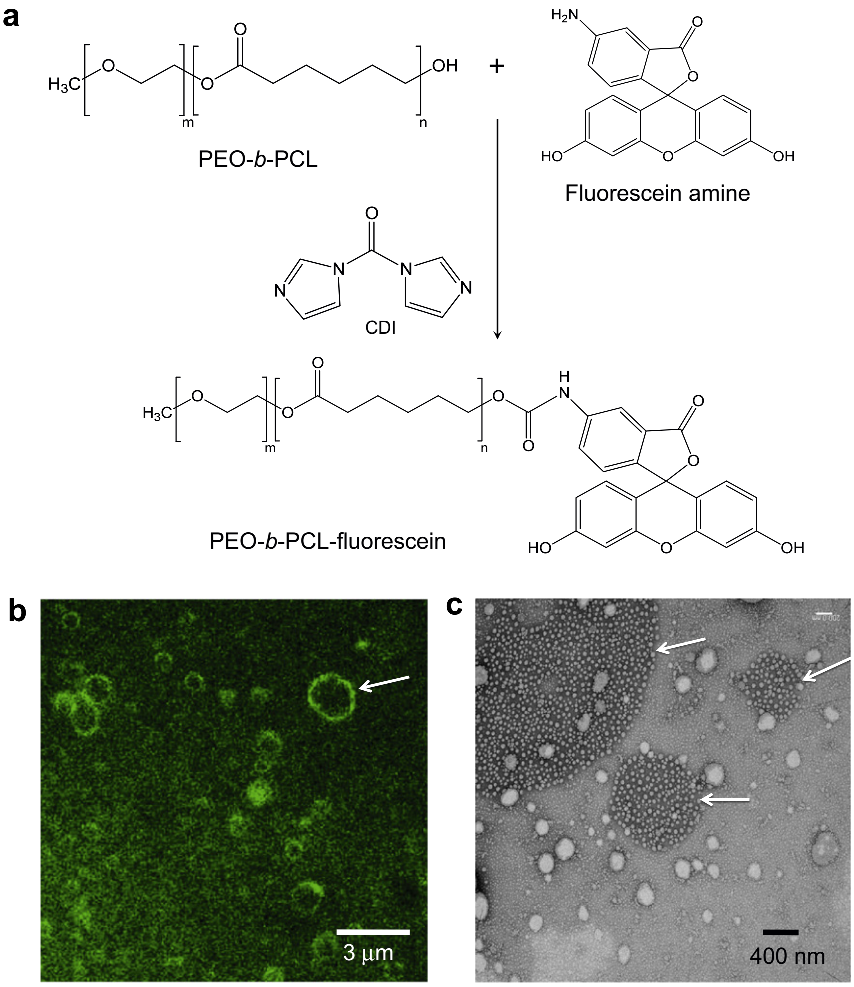

Fig. 2. (a) Synthetic scheme of the conjugation of fluorescein amine to PEO-*b*-PCL using CDI. (b) Confocal fluorescence micrograph, and (c) TEM image of the emulsions stabilized by PEO-*b*-PCL.

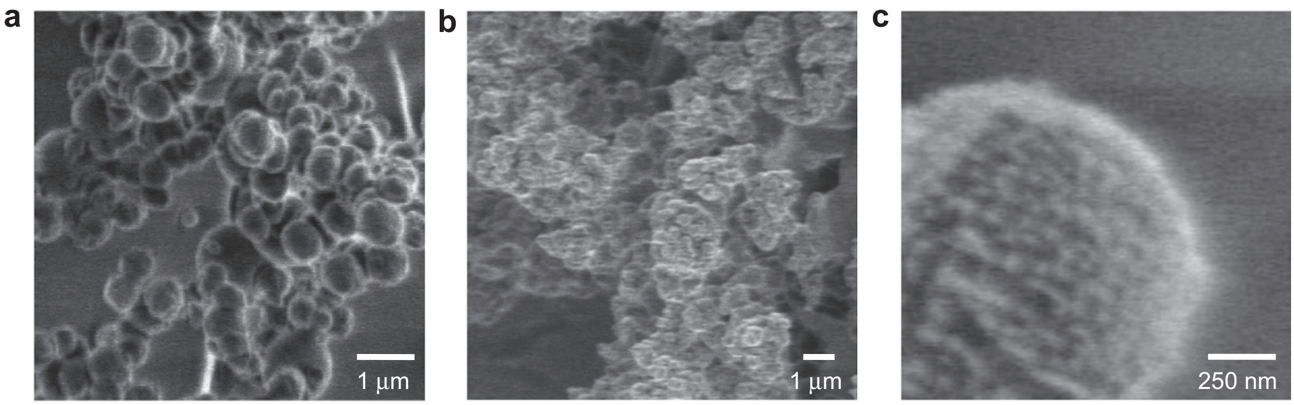

Fig. 3. Cryogenic scanning electron micrographs of the emulsions stabilized by Pluronic F127 (a) and PEO-*b*-PCL (b and c).

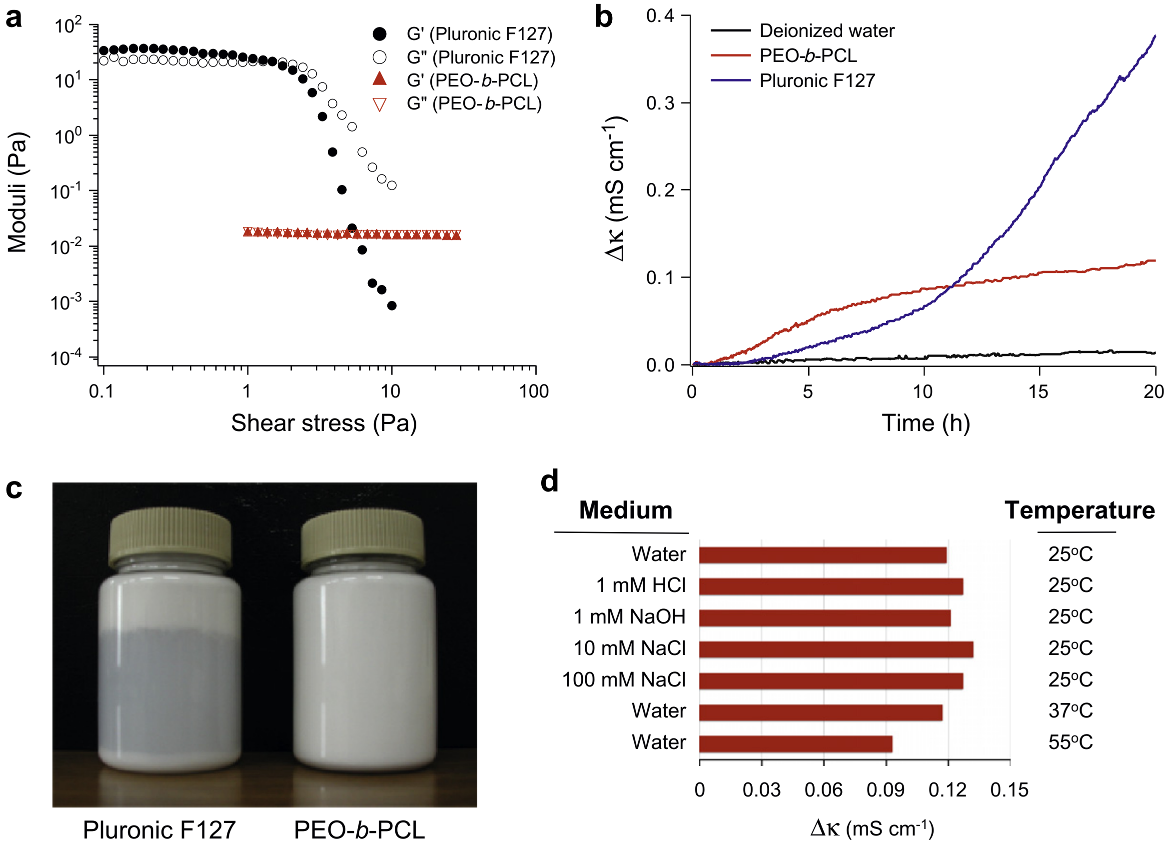

Fig. 4. Physical stability of the silicone oil emulsions stabilized by Pluronic F127 and PEO-*b*-PCL: (a) viscosity vs. shear stress sweep profiles, (b) temporal variations of the conductivity difference at 45 °C, (c) photographs of the emulsions after incubation at 45 °C for 3 days (the arrow indicates the boundary of two separated phases), and (d) the conductivity difference of oil-in-water emulsions stabilized by PEO-*b*-PCL after incubation at 45 °C for 20 h. The pH, ionic strength and temperature of the emulsions were adjusted to the conditions as indicated.

The solidification of the polymer layer around oil droplets seems to result in smaller moduli and the particle-like behavior because of the minimal deformation of the interfacial layers with shear forces.

To examine the physical stability of the emulsions stabilized by PEO-*b*-PCL, the variation in the voltage potential of the emulsion samples was determined using the two-point conductivity measurement (Fig. S1). The voltage potential ($\Delta\kappa$) is defined as the difference between the conductivities at the top (κ_1) and at the bottom (κ_2) of an emulsion sample. The conductivity analysis was very sensitive to the structural variations of emulsions so that a significant change of $\Delta\kappa$ could be measured even in case no apparent phase separation was observed. Fig. 4b shows the potential changes of the prepared emulsions monitored over time at 45 °C. During the first 11 h, the emulsions stabilized by Pluronic F127 exhibited potential values lower than those by PEO-*b*-PCL, but showed the abrupt increase of the bottom conductivity while the upper conductivity slowly decreased, resulting in the increase of the voltage potential. This result indicates that the oil droplets moved toward the upper region as a result of the increased droplet sizes. Such flocculation was apparently observed after incubation of the emulsions at 45 °C for 3 days (Fig. 4c). In contrast, the voltage potential of the emulsions stabilized by PEO-*b*-PCL gradually increased and reached a plateau value around $\Delta\kappa = 0.1\ \text{mS cm}^{-1}$, indicating the smaller change in chemical composition, under the same conditions. The emulsions stabilized by PEO-*b*-PCL started to show a slight flocculation after the incubation at 45 °C for about a week. The physical stability of the prepared emulsions was also evaluated against external stresses, including variations in pH, ionic strength, and temperature. Fig. 4d shows the voltage potentials of the emulsions stabilized by PEO-*b*-PCL after the incubation at 45 °C for 20 h. The emulsions exhibited relatively small changes around $\Delta\kappa = 0.1\ \text{mS cm}^{-1}$ in the potentials under all of the examined conditions. These results indicate that the emulsions stabilized by PEO-*b*-PCL can be very stable under a wide range of conditions.

4. Conclusions

This study has demonstrated that amphiphilic block copolymer having a hydrophobic segment not soluble in the organic phase can be utilized to very effectively stabilize emulsions, and even have the better physical stability of emulsions under various experimental conditions. PEO-*b*-PCL dissolved in silicone oil at 70 °C was dispersed in water containing no other emulsifiers. The block copolymer, originally dissolved in the organic phase, migrated toward the oil–water interface and was frozen as a mechanically robust, semi-solid polymer-rich interphase. The emulsions stabilized by PEO-*b*-PCL were very stable against heat and chemical fluctuation, under which conditions commercial polymer emulsifiers (e.g., Pluronic F127) suffered from physical instability because of the structural change of the assembled molecules. This effective emulsion stabilization implies that the emulsification approach has wide promising applications for pharmaceutical, food, and personal care and cosmetics products, which require excellent emulsion stability under a broad range of conditions.

Acknowledgments

We thank Mr. Seung Jae Baik for help with rheological measurements and Ms. Katherine Choi for editing the manuscript. This work was performed at Amore Pacific R&D Center and supported from Amore Pacific Corporation (Seoul, Republic of Korea).

Appendix A. Supplementary material

^{1}H nuclear magnetic resonance spectrum of PEO-*b*-PCL and a description on the two-point conductivity measurement. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.07.005.

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